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(71) Applicant: **MEDTRONIC, INC.**
Minneapolis, Minnesota 55432-3576 (US)

(72) Inventors:
- **Crespi, Ann M.**
  Minneapolis, Minnesota 55410 (US)
- **Chen, Kaimin**
  New Brighton, Minnesota 55112 (US)

(74) Representative:
Golding, Louise Ann
Frank B. Dehn & Co.,
179 Queen Victoria Street
London EC4V 4EL (GB)

(54) **Silver vanadium oxide**

(57) The invention provides a method for forming CSVO without the need for flowing O_2 during its synthesis. A method of forming silver vanadium oxide in accordance with the present invention includes combining AgO with a vanadium-containing compound to form a mixture; and exposing the mixture to a sufficient temperature for a time effective to form silver vanadium oxide.

The silver vanadium oxide produced in accordance with the invention may be used in the cathodes of electrochemical cells, particularly in implantable medical devices.

EP 0 856 490 A1

Description

The present invention relates to electrochemical cells, e.g. for use in implantable medical devices. In particular, the invention relates to a method of preparing a silver vanadium oxide cathode material for use in electrochemical cells.

A plurality of electrochemical cells may be connected together to form a battery. Silver-containing materials are widely used as a cathode material in electrochemical cells. Silver-containing cathodes may typically comprise silver carbonate, silver thiocyanate, divalent silver oxide, silver bismuth oxide, copper silver vanadium oxide, and silver vanadium oxide. However, when used as the cathode material in individual electrochemical cells of a battery, some of these compounds do not exhibit ideal electrical properties. Ideal electrical properties include, for example, a low internal discharge rate (i.e. low increase in internal resistance over lifetime of the cell). A high internal discharge rate undesirably decreases the delivery capacity (i.e. the integral of current x the discharge time) of a cell. Different cathode materials contribute to different problems. For example, silver chromate undesirably contributes to a large voltage drop during high loads. Divalent silver oxide is soluble and undesirably decomposes over time. These are just a few of the problems associated with some of the above-mentioned cathode materials.

Silver vanadium oxide (SVO) is utilized as a cathode material in lithium (Li) anode electrochemical cells (and in batteries incorporating such electrochemical cells) due to its relatively high volumetric energy density (i.e. the product of capacity x average voltage divided by volume of material). This property is particularly desirable for small batteries. The size of the battery is important in implantable medical devices, e.g. implantable cardiac defibrillators (such as that illustrated in Figure 1 attached hereto) so that the device itself occupies a small volume within a patient's body and is light in weight.

SVO may be prepared using a variety of known methods. These generally fall into two categories, depending on the type of chemical reaction used to produce the SVO. SVO can be synthesized using a decomposition reaction, resulting in decomposition-produced SVO (DSVO). Decomposition reactions are known to utilize decomposable metal compounds, which include nitrates, nitrites, carbonates, and ammonium salts of the reacting metal components. A conventional DSVO reaction may comprise the reaction of silver nitrate and vanadium pentoxide according to the following equation:

$$2\ AgNO_3 + 2\ V_2O_5 \rightarrow Ag_2V_4O_{11} + 2NO_x.$$

However, many conventional DSVO reactions, including the above-mentioned reaction, are undesirable due to the by-products that they produce, such as NO_x, which can be toxic at certain levels.

Alternatively, SVO can be prepared by a combination reaction, resulting in combination-produced SVO (CSVO). CSVO is characterized by a more crystalline structure, which, when compared to DSVO, contributes to its superior electrical performance in electrochemical cells. Many different silver-containing compounds have been used as reactants in such combination reactions, including $AgVO_3$, Ag_2O, and Ag(0). As described in US-A-5,221,453 (Crespi), a conventional CSVO may be produced by the reaction of silver oxide and vanadium pentoxide at a temperature of about 500°C according to the following equation:

$$Ag_2O + 2\ V_2O_5 \rightarrow Ag_2V_4O_{11}.$$

US-A-5,221,453 also discloses the use of flowing oxygen (O_2) gas and Ag(0) according to the following combination reaction:

$$2\ Ag + 2\ V_2O_5 + 0.5\ O_2 \rightarrow Ag_2V_4O_{11}.$$

Flowing O_2 is used to produce CSVO having a superior electrical performance compared to CSVO produced in the presence of flowing or stagnant (i.e. having no active gas flow) air. The need for flowing O_2, however, requires the use of a sealed retort, a tank of pure oxygen, and a flowmeter, all of which add expense to the synthesis process.

Other documents concerned with methods for the preparation of silver vanadium oxide (SVO) and electrochemical cells containing SVO cathodes, as well as electrochemical cells in general, include US-A-4,016,338 (Lauck), US-A-4,158,722 (Lauck et al.), US-A-4,310,609 (Liang et al.), US-A-4,391,729 (Liang et al.), US-A-4,542,083 (Cava et al.), US-A-4,675,260 (Sakurai et al.), 4,751,157 (Uchiyama et al.), US-A-4,751,158 (Uchiyama et al.), US-A-4,803,137 (Miyazaki et al.), US-A-4,830,940 (Keister et al.), US-A-4,964,877 (Keister et al.), US-A-4,965,151 (Takeda et al.), US-A-5,194,342 (Bito et al.), US-A-5,221,453 (Crespi), US-A-5,298,349 (Takeuchi), US-A-5,389,472 (Takeuchi et al.), US-A-5,439,760 (Howard et al.), US-A-5,545,497 (Takeuchi et al.), US-A-5,458,997 (Crespi et al.), US-A-5,472,810 (Takeuchi et al.), US-A-5,498,494 (Takeuchi et al.), US-A-5,498,495 (Takeda et al.), US-A-5,512,214 (Koksbang), US-A-5,516,340 (Takeuchi et al.), US-A-5,558,680 (Takeuchi et al.), US-A-5,567,538 (Oltman et al.), Leising et al., Chem. of Materials 5: 738-42 (1993), and Zandbergen et al., Journal of Solid State Chemistry 110: 167-175 (1994).

There is a continuing need for alternative methods for preparing a SVO material. In particular, there exists a need to reduce the expense associated with conventional methods for the synthesis of SVO, whilst at the same time providing a material which exhibits superior electrical performance when used as a cathode in an electrochemical cell. More particularly, there exists a

need for an improved method for forming CSVO material for use in the cathodes of electrochemical cells, particularly for use in implantable medical devices.

The applicants have devised an alternative method for the synthesis of a silver vanadium oxide, in particular a method which may be carried out in the absence of flowing O_2.

Viewed from one aspect the invention provides a process for the preparation of a silver vanadium oxide, said method comprising the steps of:

(a) combining AgO with a vanadium-containing compound whereby to form a mixture; and
(b) heating said mixture whereby to form a silver vanadium oxide.

In a preferred embodiment step (a) comprises combining AgO with a vanadium-containing compound and a compound selected from Ag(0), Ag_2O, and mixtures thereof whereby to form a mixture.

Viewed from a further aspect the invention provides a silver vanadium oxide composition for use in an electrochemical cell, said composition comprising silver vanadium oxide prepared by a process comprising:

(a) combining AgO with a vanadium-containing compound, optionally together with Ag(0) and/or Ag_2O, whereby to form a mixture; and
(b) heating said mixture whereby to form a silver vanadium oxide.

The method of the present invention comprises combining AgO with a vanadium-containing compound to form a mixture; and exposing the mixture to a sufficient temperature for a time effective to form silver vanadium oxide. By not requiring flowing O_2, the present invention does not require the use of a sealed retort, a tank of pure oxygen, and a flowmeter, all of which add expense to the synthesis process. Thus, the present invention can reduce the expense associated with the synthesis of CSVO, while providing a material that exhibits superior electrical performance when used as a cathode in an electrochemical cell.

In another aspect the invention provides the use as a cathode material for an electrochemical cell of a silver vanadium oxide composition as herein described.

In a yet further aspect the invention provides a cathode member for an electrochemical cell, characterised in that said member comprises a silver vanadium oxide composition as herein described.

Preferred embodiments of the invention will now be described with reference to the accompanying drawings in which:

Figure 1 is a schematic representation of an implantable battery in accordance with the present invention, e.g. for use in an implantable cardiac defibrillator.

Figure 2A is an XRD scan (Cu Kα radiation) of conventional CSVO synthesized using Ag_2O in flowing O_2.

Figure 2B is an XRD scan (Cu Kα radiation) of CSVO synthesized using AgO in stagnant air according to the present invention.

Figure 2C is an XRD scan (Cu Kα radiation) of CSVO synthesized using AgO in flowing O_2 according to the present invention.

Figure 3 is a schematic representation of an electrochemical button cell in accordance with the present invention.

Figure 4A is a partially cut-away side view of a cathode assembly incorporating CSVO synthesized according to the present invention.

Figure 4B is a partially cut-away side view of an anode assembly used with the cathode assembly of Figure 4A.

Figure 4C is a perspective view of a single cell battery incorporating CSVO synthesized according to the present invention.

Figure 5 is a graphical representation of background voltage versus capacity density for discharge curves of electrochemical cells utilizing cathode material made according to the present invention and tested at 37°C and a 28 kΩ load.

The present invention provides a method for synthesizing silver vanadium oxide (SVO) useful as a cathode material in an electrochemical cell. The method of the present invention synthesizes SVO from AgO and a vanadium-containing compound. Preferably, the SVO produced in accordance with the present invention has the formula, $Ag_xV_4O_y$, wherein x is about 1.6 to about 2.2 and y is about 10.5 to about 11.5. More preferably, x is about 2 and y is about 11. Yet more preferably, the SVO produced in accordance with the invention has the formula $Ag_2V_4O_{11}$. The resulting SVO is preferably substantially fully oxygenated. Whilst not wishing to be bound by theory, this is believed to contribute to its superior electrical performance when used as the cathode material in an electrochemical cell.

According to the present invention, AgO is used instead of Ag_2O conventionally used in SVO synthesis. Conveniently, the use of AgO allows for the use of a stagnant atmosphere instead of flowing oxygen gas when preparing the SVO. This is advantageous because it simplifies the equipment needed for carrying out the synthesis, and also reduces the cost of the synthesis of SVO. The method of the present invention can actually be carried out in a simple box furnace with no atmosphere control. As described herein, the method of the invention may nevertheless be carried out in the presence of a flowing gas, e.g. O_2.

The reaction between AgO and a vanadium-containing compound may produce oxygen as a by-product, which can contribute to producing fully oxygenated SVO. Thus, the O_2 by-product can help form and main-

tain a high oxidation state of the SVO, which in turn improves the performance of batteries containing SVO cathodes. The O_2 by-product is utilized in the reaction to raise the partial pressure of O_2 in the synthesis reaction chamber, allowing for the use of environments that are initially low in O_2 content.

Significantly, the AgO can be combined with the vanadium-containing compound in a variety of atmospheres. For example, the reaction can take place in the presence of a gas, such as oxygen (O_2), nitrogen (N_2), argon (Ar), atmospheric air, or mixtures thereof. The gas can be stagnant or flowing. Preferably, the gas is stagnant, to avoid the need for expensive gas flow equipment. More preferably, the gas is atmospheric air, to avoid the need for expensive O_2 flowing equipment. Although it is understood that stagnant air is preferred, thereby allowing for the use of simplified equipment, the method of the present invention is also advantageous because it can produce high quality SVO in a variety of atmospheres.

The vanadium-containing compound can be, for example, NH_4VO_3, VO_2, V_2O_3, V_2O_5, V_2O_4, V_3O_7, V_4O_9, V_6O_{13}, or mixtures thereof. Preferably, the vanadium-containing compound is V_2O_5 or V_6O_{13}. More preferably, the vanadium-containing compound is V_2O_5. When V_2O_5 is used as the vanadium-containing compound, the following equation is representative of the reaction:

$$2\ AgO + 2\ V_2O_5 \rightarrow Ag_2V_4O_{11} + 0.5\ O_2.$$

The use of AgO in the method of the present invention allows for the use of compounds in which the vanadium is in a lower oxidation state, as compared to vanadium in V_2O_5. The use of lower oxidation state vanadium may result in slightly different crystallographic and electrical properties of the resulting SVO. Thus, VO_2, V_2O_3, V_2O_4, V_3O_7, V_4O_9, V_6O_{13}, or mixtures thereof, can also be used, in which the vanadium exists in a lower oxidation state than in V_2O_5. The following equations are representative of methods in which SVO having the formula, $Ag_2V_4O_{11}$, is formed from lower oxidation state vanadium in the presence of O_2 gas:

$$2\ AgO + 4\ VO_2 + 1/2\ O_2 \rightarrow Ag_2V_4O_{11};$$

$$2\ AgO + 2/3\ V_6O_{13} + 1/6\ O_2 \rightarrow Ag_2V_4O_{11};$$

$$2\ AgO + V_4O_9 \rightarrow Ag_2V_4O_{11};$$

and

$$AgO + 4/3\ V_3O_7 \rightarrow Ag_2V_4O_{11} + 1/6\ O_2.$$

However, variations to the above equations can also yield mixed valence SVO in accordance with the present invention.

According to another aspect of the present invention, a mixture of AgO and Ag_2O can be used to produce SVO. This allows SVO-producing reactions to be tailored to produce desired by-products and allows the use of desired reactants. If oxygen flowing equipment is available, for example, the reaction can be tailored to utilize O_2 as a reactant. However, it is preferable to be able to synthesise SVO in the presence of stagnant air. Some examples of preferred equations in accordance with this aspect of the invention include:

$$2\ AgO + Ag_2O + 4V_2O_5 \rightarrow Ag_2V_4O_{11} + ½\ O_2;$$

and

$$2\ AgO + 3\ Ag_2O + 8\ V_2O_5 \rightarrow Ag_2V_4O_{11} + ½\ O_2.$$

According to yet another aspect of the present invention, a mixture of AgO and Ag(0) can be used to produce SVO. Again, this allows SVO-producing reactions to be tailored to produce desired by-products and allows the use of desired reactants. Furthermore, a mixture of AgO, Ag(0), and Ag_2O can also be used to produce SVO.

The AgO, and optionally Ag_2O and/or Ag(0), and the vanadium-containing compound(s) are intimately mixed and then exposed to a sufficient temperature for a time effective to produce silver vanadium oxide. Preferably, the reactants are ground together to reduce their particle size and produce a substantially homogeneous mixture. Depending on the desired SVO product, the mixture includes a sufficient molar ratio of silver to vanadium atoms. This molar ratio can vary depending on the vanadium-containing compound and the presence of Ag_2O and/or Ag(0) in addition to the AgO. For example, if V_2O_5 is used with AgO, these two reactants are used in approximately equimolar amounts. If, however, V_4O_9 is used with AgO, these two reactants are used in a respective equimolar ratio of 1:2 according to the following equation:

$$2\ AgO + V_4O_9 \rightarrow Ag_2V_4O_{11}.$$

The temperature to which the mixture produced in step (a) is exposed is preferably about 400°C to about 600°C. When SVO having the formula $Ag_2V_4O_{11}$ is produced, the temperature is preferably at least about 440°C, and more preferably at least about 480°C. It is also preferably no greater than about 550°C, and more preferably no greater than about 530°C. Preferably, the mixture is held at the desired temperature for at least about 1 hour, and more preferably for at least about 4 hours. Typically, it can be held at the desired temperature for about 24 hours or longer, although it is preferably held at the desired temperature for no greater than about 8 hours. The time can be extended beyond 24 hours without degrading the resultant SVO, particularly if the reaction is carried out in an O_2 atmosphere, although there is typically no advantage to doing so.

After the SVO is synthesized in accordance with reactions of the present invention, the SVO can be ground to provide a smaller particle size. Any conventional method for breaking materials into loose particles can be used to grind the materials. For example, material can be broken into loose particles using a mortar and pestle. There is no need for purification of the material after it is formed.

XRD measurements are one way of characterizing the resulting SVO material. Using Bragg's law, $n\lambda = 2d_{hkl}\sin\theta$, the size and shape of a unit cell can be determined from the XRD data. In Bragg's law, the wavelength of an incident beam is represented as λ and n is a constant, corresponding to an integral number of λs. The angle of incidence of an incident beam on a substrate is represented as θ. The distance between crystallographic planes is represented as d_{hkl}. The distance between crystallographic planes, hkl, corresponds to the lattice parameter of a material (i.e. the spacing between adjacent atoms within a crystallographic plane defined by the parameters, hkl). Depending on the crystallographic structure of a material, not every incident beam will be reflected, as neighbouring diffracted rays can cancel each other out. The angle of incidence can be varied to determine the distance between crystallographic planes, d_{hkl}. Furthermore, by analyzing the intensity of diffracted beams, the distribution of two or more atoms at each lattice point can be determined.

For comparison, a conventional CSVO XRD scan (Cu Kα radiation) is illustrated in Figure 2A. CSVO of Figure 2A was synthesized in flowing O_2 at a temperature of 520°C for 6 hours, according to the following equation:

$$Ag_2O + 2V_2O_5 \rightarrow Ag_2V_4O_{11}.$$

One CSVO XRD peak 80 is indexed on a C-centered monoclinic cell at about 23.6° (2θ), which corresponds to a {002} crystallographic plane. Another peak 82 is indexed on a C-centered monoclinic cell at about 24.0° (2θ), which corresponds to a {201} crystallographic plane. Because XRD analysis is indicative of the crystal structure of a material, it is desirable to have two resolvable peaks 80 and 82 at about 23° (2θ) to about 25° (2θ) in an SVO XRD scan because this indicates the high degree of crystallinity that is characteristic of conventional CSVO.

Figure 2B is an XRD scan (Cu Kα radiation) of CSVO synthesized at a temperature of 520°C for 6 hours according to the following equation:

$$2\ AgO + 2\ V_2O_5 \rightarrow Ag_2V_4O_{11} + 0.5\ O_2.$$

Stagnant air was used in the processing chamber, without any flowing gases. Figure 2C is an XRD scan (Cu Kα radiation) of CSVO synthesized at a temperature of 520°C for 6 hours according to the following equation:

$$2\ AgO + 2\ V_2O_5 \rightarrow Ag_2V_4O_{11} + 0.5\ O_2.$$

Flowing O_2 was used in the processing chamber. Both XRD scans (Figures 2B and 2C) for CSVO synthesized in accordance with the present invention are substantially similar to the XRD scan (Figure 2A) for conventional CSVO. Thus, the new method of synthesis described herein provides CSVO similar to CSVO synthesized using Ag_2O.

SVO prepared in accordance with the method of the present invention is advantageously used as the cathode material in an electrochemical cell. In a further aspect the invention thus provides a process as hereinbefore described further comprising the steps of:

forming a cathode comprising the silver vanadium oxide;
providing an anode;
providing an electrolyte; and assembling the cathode, the anode, and the electrolyte into an electrochemical cell.

Conveniently, the silver vanadium oxide material is combined with a binder and a conductivity enhancer to form a cathode material. A cathode is then formed from the cathode material and, together with the anode and a separator this is then placed in a can. An electrolyte may then be introduced into the can. Alternatively, the cathode material combination step may comprise the step of adding an electrolyte to the cathode material. The step of sealing the can to form the cell can be effected once the cathode, the anode and the separator have been disposed therewithin.

Figure 3 illustrates a representative electrochemical button cell. An electrochemical cell 100 comprises a cathode 102 and an anode 104 encased in an anode can 106, which is typically formed of metal, such as titanium or stainless steel. A conventional cap 108, for example one made of a nickel/steel/copper alloy, conventional seals 110, for example one made of plastic, and a conventional membrane 112 made of a semi-permeable material, are also typically utilized in the cell 100. An electrolyte 114 separates the anode 104 and the cathode 102. The electrolyte 114 may comprise an organic or inorganic material, and may be in either the solid or liquid state.

An electrochemical cell 100 operates by developing a differential electrical potential between the cathod 102 and the anode 104. The anode 104 oxidizes to form metal ions during discharge of the cell 100. Li is preferred as the anode 104 material due to its strong electropositivity. However, other metals can be used for the anode 104 material, including calcium, magnesium, aluminum, and zinc. The cathode 102 converts the metal ions to atomic or molecular forms, thereby conducting an electrical current through the cell 100.

Typically, to form the cathode 102 from the SVO, the SVO is pressed into a desired configuration, such as a

pressed, cylindrical-shaped pellet, using conventional techniques. For example, the SVO can be dry-pressed or pressed with a small addition of, for example, a liquid electrolyte, a binder (e.g. polytetrafluoroethylene, methyl cellulose, ethyene propylene diene terpolymer (EPDM), polyethylene, polypropylene, polyolefins, fluorinated ethylene propylene (FEP), polyvinylidene fluoride, or mixtures thereof), a conductor (e.g. graphite powder, carbon black, acetylene black powder, or mixtures thereof), and a surfactant. A wide variety of other additives may also be added to the SVO prior to pressing it into the desired configuration.

A plurality of electrochemical cells can be connected to form an electrode assembly in a battery. The SVO cathode material made according to the method of the present invention can be incorporated into a wide variety of batteries, such as, for example, those described in US-A-5,458,997 (Crespi et al.), US-A-4,830,940 (Keister et al.), US-A-4,964,877 (Keister et al.), and US-A-5,439,760 (Howard et al.).

A specific example of an electrochemical cell in a single-cell battery is shown in Figure 4C, the cathode and anode of which are shown in Figures 4A and 4B, respectively. In this embodiment, a coiled electrode assembly comprised of elongated anode and cathode sub-assemblies pressed onto a metal current collector and enveloped with a separator of microporous material are overlaid with respect to each other and coiled up. Further details of this cell are provided in US-A-5,439,760 (Howard et al.).

Briefly, with respect to Figure 4A, which shows an elongated cathode assembly 120, the anode assembly 120 includes a current collector 121 (e.g. titanium, stainless steel, or another conductive metal which is corrosion-resistant when associated with the cathode material), onto which two layers of a cathode material containing SVO are pressed. Only one layer of this cathode material (123) is shown in Figure 4A. The other layer is on the opposite side of the current collector 121. The SVO is typically combined with a binder, such as polytetrafluoroethylene, along with carbon black and graphite as conductivity enhancers, dried to a desired moisture content, placed in a uniform layer over the curr nt collector 121, and then dried to form each of the cathode material layers (e.g. 123). Connector tabs 138 project from the edge of the current collector 121.

Briefly, with respect to Figure 4B, which shows an elongated anode assembly 130, anode assembly 130 includes a screen current collector 131 (e.g. nickel, copper, or another conductive metal which is corrosion-resistant when associated with the alkali metal), which has a first layer of alkali metal 132 on one side and a second layer of alkali metal on the opposite side (not shown). The alkali metal is preferably lithium metal or an alloy of lithium pressed onto the screen current collector 131. In this embodiment, the anode assembly 130 has at one end 133 only alkali metal 132. The bare portion of the current collector 131 will extend from the outer wrap of the wound electrode assembly as no active material is required for that surface. Connector tabs 142 project from the edge of the current collector 131.

To further complete the assembly of one embodiment of a battery in accordance with the present invention, each of the anode and cathode structures in the electrode assembly 140 is typically encased in a separator material, such as polypropylene or polyethylene, as is further discussed in US-A-5,439,760 (Howard et al.). A coil insulator 144 is then placed over the electrode assembly 140. The coil insulator 144 includes a notch 146 and a slit 148 to accommodate anode lead portions 142. The coil insulator 144 further includes slits 150 and 152 to accommodate cathode lead portions 138. The electrode assembly 140 is inserted in an insulative case liner 154, which is then inserted in a case 156. The insulative case liner 154 preferably extends at its top edge above the edge of the electrode assembly 131 in order to provide an overlap with other insulative elements. It may also include a notch 158 on one side in order to allow easy connection of the anode lead portions 142 to the case 156. The coil insulator 144 and case liner 154 are preferably made from a polyolefin polymer or a fluoropolymer, such as ethylene tetrafluoroethylene copolymer (ETFE). The case 156 is preferably made of stainless steel or titanium.

It is to be understood that many other battery configurations can be formed with the improved cathode material in accordance with the present invention.

Electrochemical cells according to the present invention can be used in batteries such as those utilized in implantable cardiac defibrillators 160, as illustrated in Figure 1.

Figure 1 illustrates a defibrillator and lead set according to the present invention. The ventricular lead comprises an elongated insulative lead body 16, carrying three concentric coiled conductors, separated from one another by tubular insulative sheaths. Located adjacent the distal end of the lead are a ring electrode 24, an extendible helix electrode 26 mounted retractably within an insulative electrode head 28, and an elongated coil electrode 20. Each of the electrodes is coupled to one of the coiled conductors within lead body 16. Electrodes 24 and 26 are employed for cardiac pacing and for sensing ventricular depolarizations. At the proximal end of the lead is a bifurcated connector 14 which carries three electrical connectors, each coupled to one of the coiled conductors. The defibrillation electrode 20 may be fabricated from platinum, platinum alloy or other materials known to be suitable for use in implantable defibrillation electrodes and may be about 5 cm in length.

The atrial/SVC lead comprises an elongated insulative lead body 15, carrying three concentric coiled conductors, separated from one another by tubular insulative sheaths, corresponding to the structure of the ventricular lead. Located adjacent the J-shaped distal end of the lead are a ring electrode 21 and an extendible helix electrode 17, mounted retractably within an

insulative electrode head 19. Each of the electrodes is coupled to one of the coiled conductors within the lead body 15. Electrodes 17 and 21 are employed for atrial pacing and for sensing atrial depolarizations. An elongated coil electrode 23 is provided, proximal to electrode 21 and coupled to the third conductor within the lead body 15. Electrode 23 preferably is about 10 cm in length or greater and is configured to extend from the SVC toward the tricuspid valve. Conveniently, approximately 5 cm of the right atrium/SVC electrode may be located in the right atrium, with the remaining 5 cm located in the SVC. At the proximal end of the lead is a bifurcated connector 13 which carries three electrical connectors, each coupled to one of the coiled conductors.

The coronary sinus lead comprises an elongated insulative lead body 6, carrying one coiled conductor, coupled to an elongated coiled defibrillation electrode 8. Electrode 8, illustrated in broken outline, is located within the coronary sinus and great vein of the heart. At the proximal end of the lead is a connector plug 4 which carries an electrical connector, coupled to the coiled conductor. The coronary sinus/great vein electrode 8 may be about 5 cm in length.

An implantable pacemaker/cardioverter/defibrillator 10 is shown in combination with the leads, with the lead connector assemblies 4, 13 and 14 inserted into the connector block 12. Optionally, insulation of the outward facing portion of the housing 11 of the pacemaker/cardioverter/defibrillator 10 may be provided using a plastic coating which may comprise, for example, parylene or silicone rubber, as is currently employed in some unipolar cardiac pacemakers. However, the outward facing portion may instead be left uninsulated, or some other division between insulated and uninsulated portions may be employed. The uninsulated portion of the housing 11 optionally serves as a subcutaneous defibrillation electrode, used to defibrillate either the atria or ventricles. Other lead configurations and electrode locations may of course be substituted for the lead set illustrated. For example, atrial defibrillation and sensing electrodes might be added to either the coronary sinus lead or the right ventricular lead instead of being located on a separate atrial lead, thereby allowing for a two-lead system.

The present invention provides a method for forming CSVO having superior electrical performance without the need for flowing O_2 during its synthesis. The SVO material in accordance with the invention is suitable for use in the cathodes of electrochemical cells, particularly for use in implantable medical devices, e.g. cardiac defibrillators.

Alternatively, the silver vanadium oxide material prepared in accordance with the invention may find further application as a ceramic material.

Specific methods and apparatus embodying the invention are described by way of the following non-limiting examples.

<u>Example 1</u>

<u>Preparation of CSVO</u>

An equimolar mixture of AgO (4.5 g) and V_2O_5 (6.6 g) was ground using a mortar and pestle to produce a homogenous mixture. The mixture was placed in an alumina crucible, which was then placed in a Lindberg furnace under air at atmospheric pressure. The reaction was then carried out at 520°C and a heating rate of 5°C/minute for 6 hours.

<u>Example 2</u>

<u>Preparation of CSVO</u>

A mixture of AgO (3.0 g) and V_6O_{13} (4.15 g) was ground using a mortar and pestle to produce a homogenous mixture. The mixture was placed in an alumina crucible, which was then placed in a Lindberg furnace under O_2 flow at a flow rate of 100 mL/minute. The reaction was then carried out at 520°C and a heating rate of 5°C/minute for 6 hours.

<u>Example 3</u>

<u>Preparation of CSVO</u>

A mixture of AgO (1.0 g), Ag_2O (0.935 g), and V_2O_5 (2.939 g) was ground using a mortar and pestle to produce a homogenous mixture. The mixture was placed in an alumina crucible, which was then placed in a Lindberg furnace under air at atmospheric pressure. The reaction was then carried out at 500°C and a heating rate of 5°C/minute for 6 hours.

<u>Example 4</u>

<u>Formation of CSVO Cathode</u>

SVO prepared in accordance with the invention was mixed with a polymeric binder (polytetrafluoroethylene), graphite powder, and carbon black. The mixture contained 91% SVO, 5% polymeric binder (polytetrafluoroethylene), 2% carbon black, and 2% graphite powder. The method of Howard et al. (see US-A-5,439,760) was then used to prepare the SVO cathode of the present invention. A disc-shaped pellet having an area on one major surface thereof of about 2.8 cm^2 was cut from th resulting sheet of cathode material to form a cathode for use in an electrochemical cell.

<u>Example 5</u>

<u>Formation of an Electrochemical Cell</u>

A pressed pellet was formed for use as the cathode in an electrochemical cell. The SVO used in the cathode

was prepared according to Example 1. The cathode contained a titanium current collector and consisted of 91% active cathode material, 5% polymer binder (polytetrafluoroethylene), 2% carbon black, and 2% graphite powder. The cathode was assembled with a lithium anode and an electrolyte consisting of 1.0 M $LiAsF_6$ in 50% by volume propylene carbonate and 50% by volume dimethoxyethane.

Example 6

Testing of Electrochemical Cells

A discharge test was conducted for an electrochemical cell made in accordance with Example 5. The results are shown by curve 170 in Figure 5. A second electrochemical cell was made in accordance with Example 5, but in which SVO was synthesized in the presence of flowing O_2 instead of atmospheric air. The discharge test for this second electrochemical cell is shown by curve 172 in Figure 5. A third electrochemical cell was made in accordance with Example 5, but a different SVO cathode material was utilized. The SVO cathode material used for this third electrochemical cell was synthesized at 520°C for 6 hours in flowing O_2 according to the conventional reaction:

$$Ag_2O + 2V_2O_5 \rightarrow Ag_2V_4O_{11}.$$

The discharge test for this third electrochemical cell is shown by curve 174 in Figure 5.

The cathode in each of the three cells contained a titanium current collector and consisted of 91% active cathode material, 5% polymer binder (polytetrafluoroethylene), 2% carbon black, and 2% graphite powder. The electrolyte was 1.0 M $LiAsF_6$ in 50% by volume propylene carbonate an 50% by volume dimethoxyethane.

The electrochemical cells were discharged at an operating temperature of 37°C with a resistive load of 28 kohms.

Comparative results are illustrated in Figure 5. Figure 5 illustrates the background voltage versus delivered capacity for the three electrochemical cells. The similarity of the three discharge curves 170, 172, and 174 indicates that all three electrochemical cells have similar capacity densities. Thus, SVO prepared in accordance with the present invention can be effectively utilized in electrochemical cells, producing equivalent electrical discharge characteristics as CSVO prepared according to conventional methods.

Example 7

X-Ray Diffraction Analysis

A Philips XPert diffractometer (Philips Electronics, Mahwa, New Jersey) was used for the measurements. The data collection time used was 8 seconds per step and a step size of 0.02° (2θ). Philips PC-APD 4.0b software was used to analyze the XRD data collected. For the XRD scans presented herein, an incident beam was deflected off a copper target having a wavelength of 1.5406 angstroms to produce Cu Kα, radiation. The angle of incidence was varied to determine the distance between crystallographic planes, d_{hkl}.

For comparison, an XRD scan (Cu Kα radiation) for a conventional CSVO is illustrated in Figure 2A. CSVO of Figure 2A was synthesized in flowing O_2 at a temperature of 520°C for 6 hours, according to the following equation:

$$Ag_2O + 2V_2O_5 \rightarrow Ag_2V_4O_{11}.$$

One CSVO XRD peak 80 was indexed on a C-centered monoclinic cell at about 23.6° (2θ), which corresponds to a {002} crystallographic plane. Another peak 82 was indexed on a C-centered monoclinic cell at about 24.0° (2θ), which corresponds to a {201} crystallographic plane. Because XRD analysis is indicative of the crystal structure of a material, it is desirable to have two resolvable peaks 80, 82 at about 23° (2θ) to about 25° (2θ) in an SVO XRD scan because this indicates the high degree of crystallinity that is characteristic of conventional CSVO.

Figure 2B is an XRD scan (Cu Kα radiation) of CSVO synthesized at a temperature of 520°C for 6 hours according to the following equation:

$$2\ AgO + 2\ V_2O_5 \rightarrow Ag_2V_4O_{11} + 0.5\ O_2.$$

Stagnant air was used in the processing chamber, without any flowing gases. Figure 2C is an XRD scan (Cu Kα radiation) of CSVO synthesized at a temperature of 520°C for 6 hours according to the following equation:

$$2\ AgO + 2\ V_2O_5 \rightarrow Ag_2V_4O_{11} + 0.5\ O_2.$$

Flowing O_2 was used in the processing chamber. Both XRD scans (Figures 2B and 2C) for CSVO synthesized in accordance with the present invention are substantially similar to the XRD scan (Figure 2A) for conventional CSVO. Thus, XRD analysis further indicates that the new method of synthesis described herein provides CSVO similar to that synthesized using Ag_2O.

Claims

1. A process for the preparation of a silver vanadium oxide, said method comprising the steps of:

   (a) combining AgO with a vanadium-containing compound whereby to form a mixture; and
   (b) heating said mixture whereby to form a silver vanadium oxide.

2. A process as claimed in claim 1, wherein step (a)

comprises combining AgO with a vanadium-containing compound and a compound selected from Ag(0), Ag_2O, and mixtures thereof whereby to form a mixture.

3. A process as claimed in claim 1 or claim 2, wherein step (b) is carried out at a temperature of at least about 440°C.

4. A process as claimed in any one of claims 1 to 3, wherein step (b) is carried out at a temperature of no greater than about 550°C.

5. A process as claimed in claim 1 or claim 2, wherein step (b) is carried out at a temperature of from about 480°C to about 530°C.

6. A process as claimed in any one of claims 1 to 5, wherein step (b) comprises heating said mixture for at least about 1 hour.

7. A process as claimed in any one of claims 1 to 5, wherein step (b) comprises heating said mixture for at least about 4 hours.

8. A process as claimed in claim 1 or claim 2, wherein step (b) comprises heating said mixture to a temperature of from about 440°C to about 550°C for about 4 to 8 hours.

9. A process as claimed in any preceding claim, wherein the vanadium-containing compound is selected from NH_4VO_3, VO_2, V_2O_3, V_2O_5, V_2O_4, V_3O_7, V_4O_9, V_6O_{13}, and mixtures thereof.

10. A process as claimed in claim 1 comprising the steps of:

    (a) combining AgO with V_2O_5 in approximately equimolar amounts whereby to form a mixture; and
    (b) heating the mixture to a temperature of from about 440°C to about 550°C for at least about 1 hour to form silver vanadium oxide.

11. A process as claimed in any preceding claim, wherein step (b) is effected in the presence of a gas selected from oxygen, nitrogen, argon, atmospheric air, and mixtures thereof.

12. A process as claimed in claim 11, wherein said gas comprises stagnant atmospheric air.

13. A silver vanadium oxide composition for use in an electrochemical cell, said composition comprising silver vanadium oxide prepared by a process comprising:

    (a) combining AgO with a vanadium-containing compound, optionally together with Ag(0) and/or Ag_2O, whereby to form a mixture; and
    (b) heating said mixture whereby to form a silver vanadium oxide.

14. A composition as claimed in claim 13, wherein said silver vanadium oxide has the formula $Ag_xV_4O_y$, wherein x is about 1.6 to about 2.2 and y is about 10.5 to about 11.5.

15. A composition as claimed in claim 14, wherein y is about 11.

16. A composition as claimed in claim 14 or claim 15, wherein x is about 2.

17. A silver vanadium oxide composition prepared by a process as claimed in any one of claims 1 to 12.

18. Use as a cathode material for an electrochemical cell of a silver vanadium oxide composition as claimed in any one of claims 13 to 17.

19. A cathode member for an electrochemical cell, characterised in that said member comprises a silver vanadium oxide composition as claimed in any one of claims 13 to 17.

20. A cathode member as claimed in claim 19, further comprising a binder material and optionally a conductivity enhancer and/or an electrolyte.

21. A cathode member as claimed in claim 20, wherein said binder material is selected from polytetrafluoroethylene, methyl cellulose, ethylene propylene diene terpolymer (EPDM), polyethylene, polypropylene, polyolefins, fluorinated ethylene propylene (FEP), polyvinylidene fluoride, and combinations or mixtures thereof.

22. A cathode member as claimed in claim 20 or claim 21, wherein said conductivity enhancer is selected from graphite powder, carbon black, acetylene black powder, and combinations or mixtures thereof.

23. A cathode member as claimed in any one of claims 20 to 22, wherein said electrolyte is selected from a liquid electrolyte, a solid electrolyte, an organic electrolyte and an inorganic electrolyte.

24. A cathode member as claimed in any one of claims 20 to 23 further comprising a surfactant.

25. A cathode member as claimed in any one of claims 20 to 24 formed into a cylindrically-shaped pellet for use in a button cell.

26. A cathode member as claimed in any one of claims 20 to 24 formed into a strip-shaped configuration for use in a spirally-wound cell.

27. An electrochemical cell comprising:

    a cathode, wherein said cathode comprises a cathode member as claimed in any one of claims 20 to 26;
    an anode; and
    an electrolyte.

28. An implantable medical device powered by an electrochemical cell as claimed in claim 27.

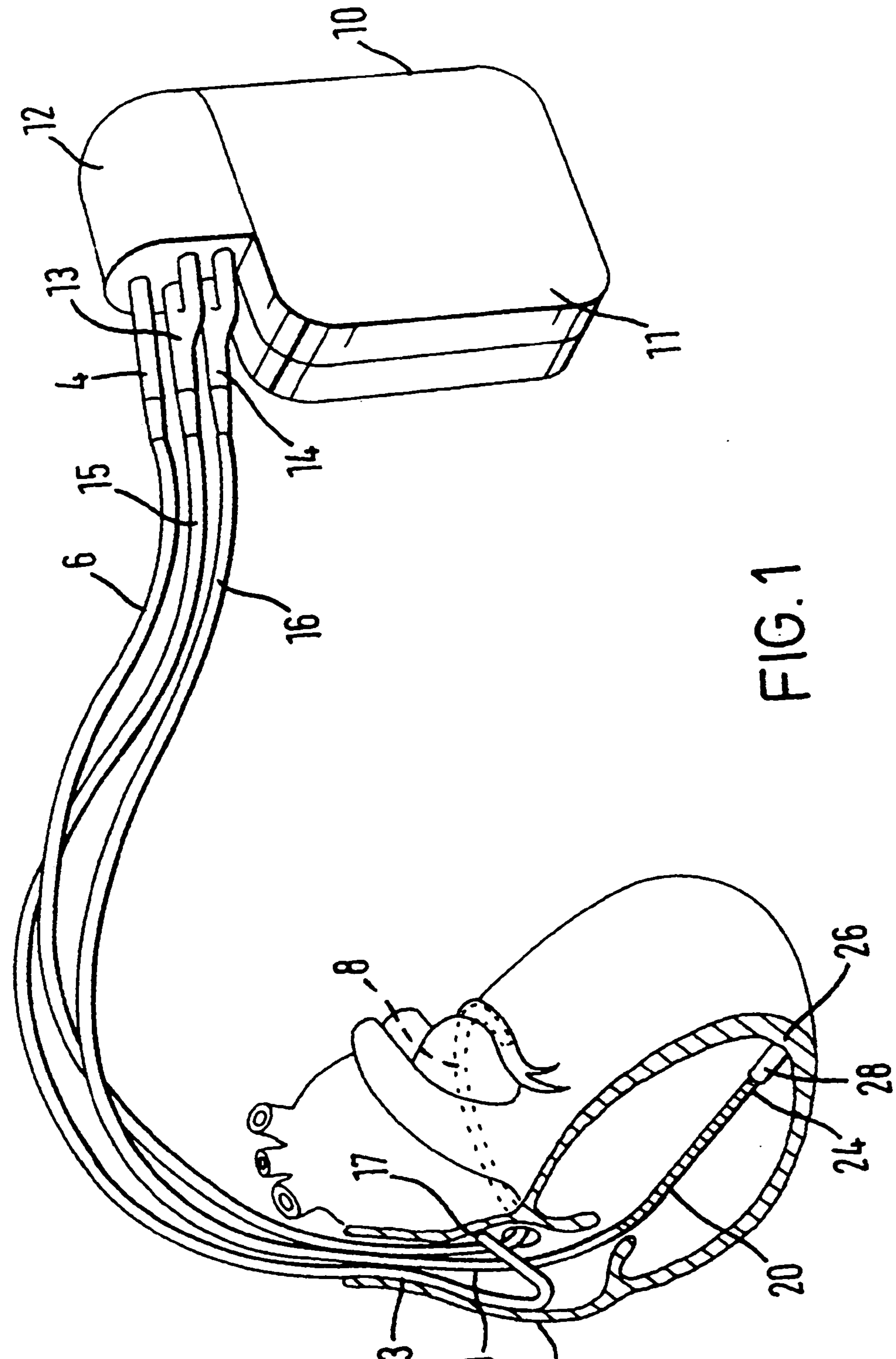


FIG. 1

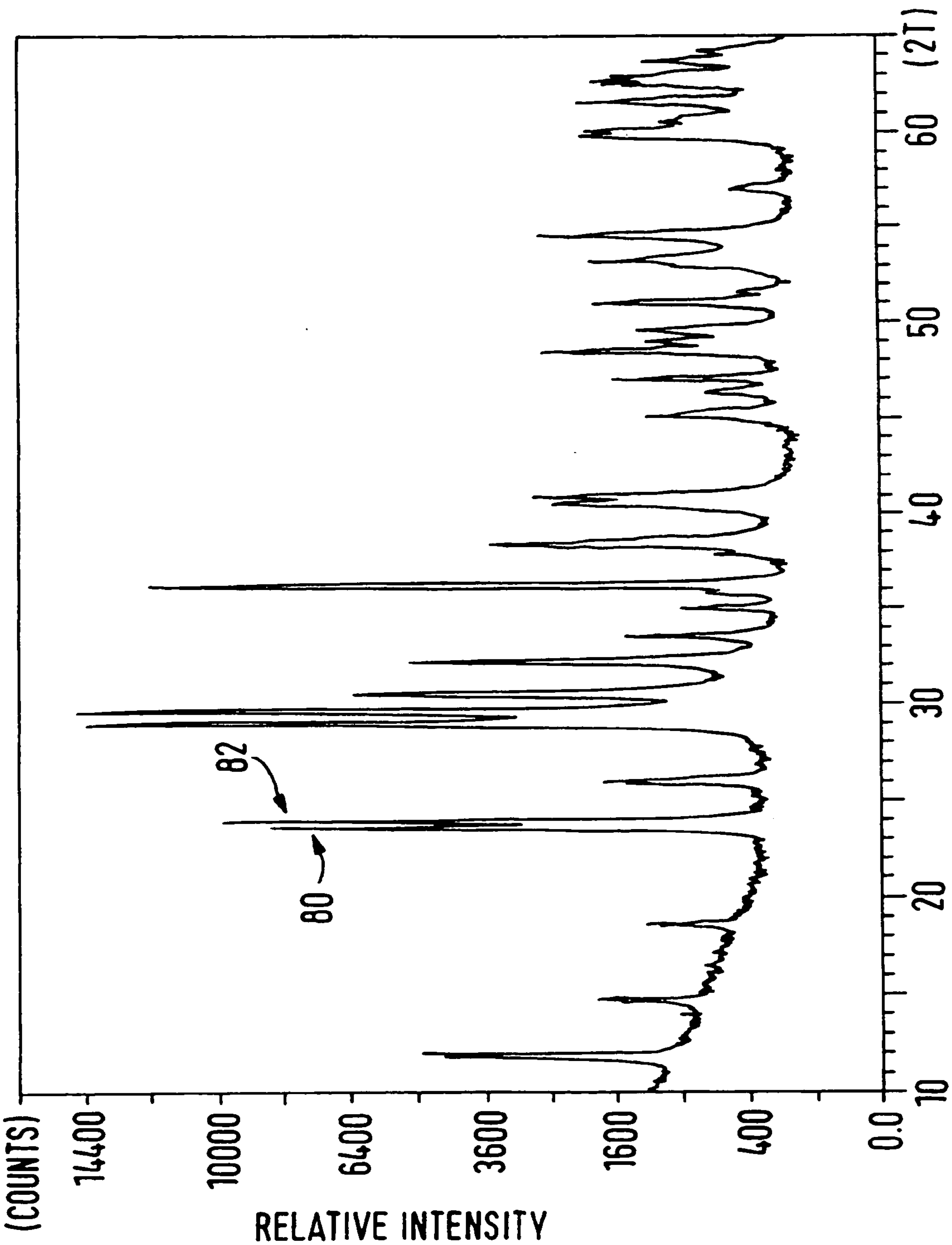
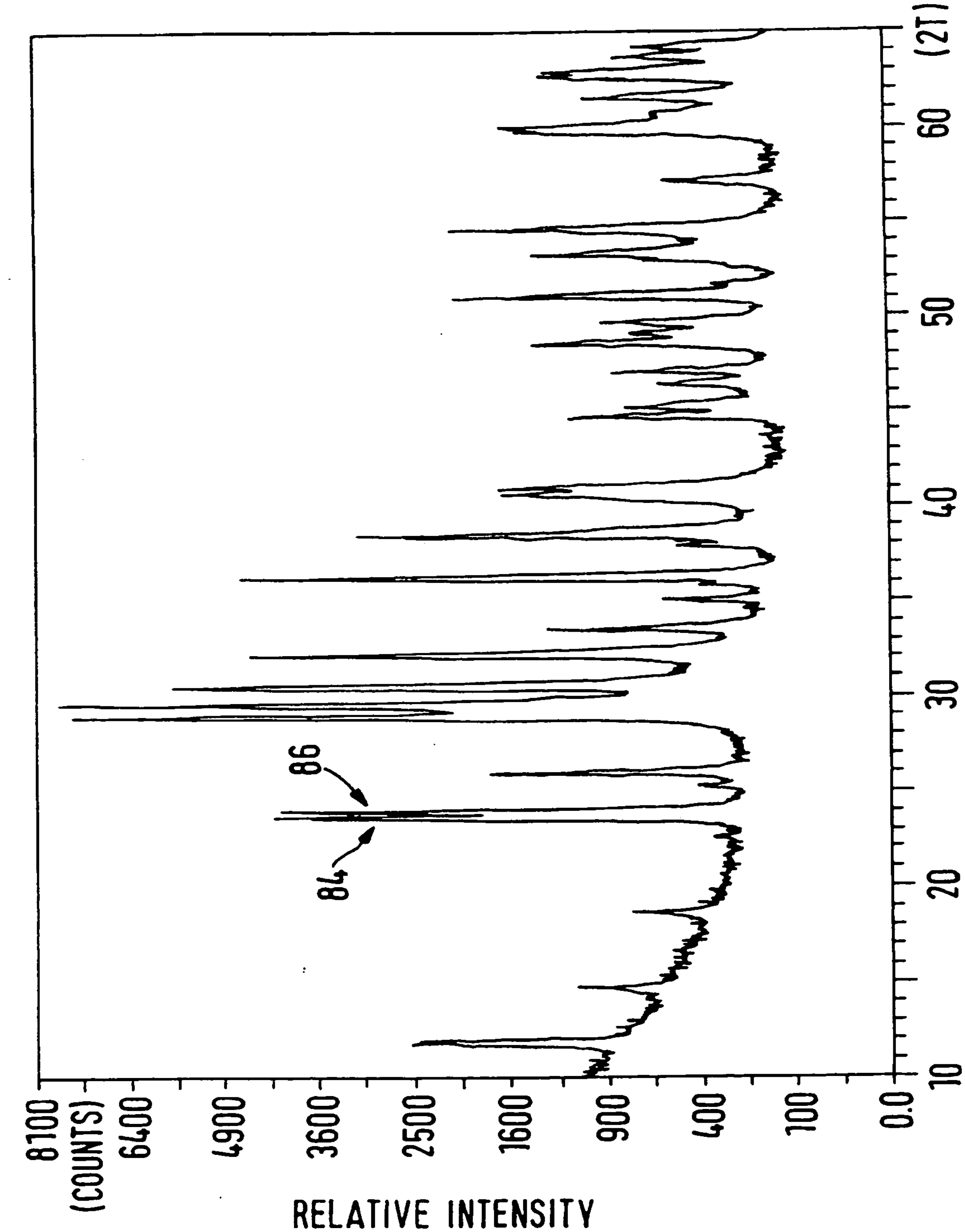


FIG. 2A (PRIOR ART)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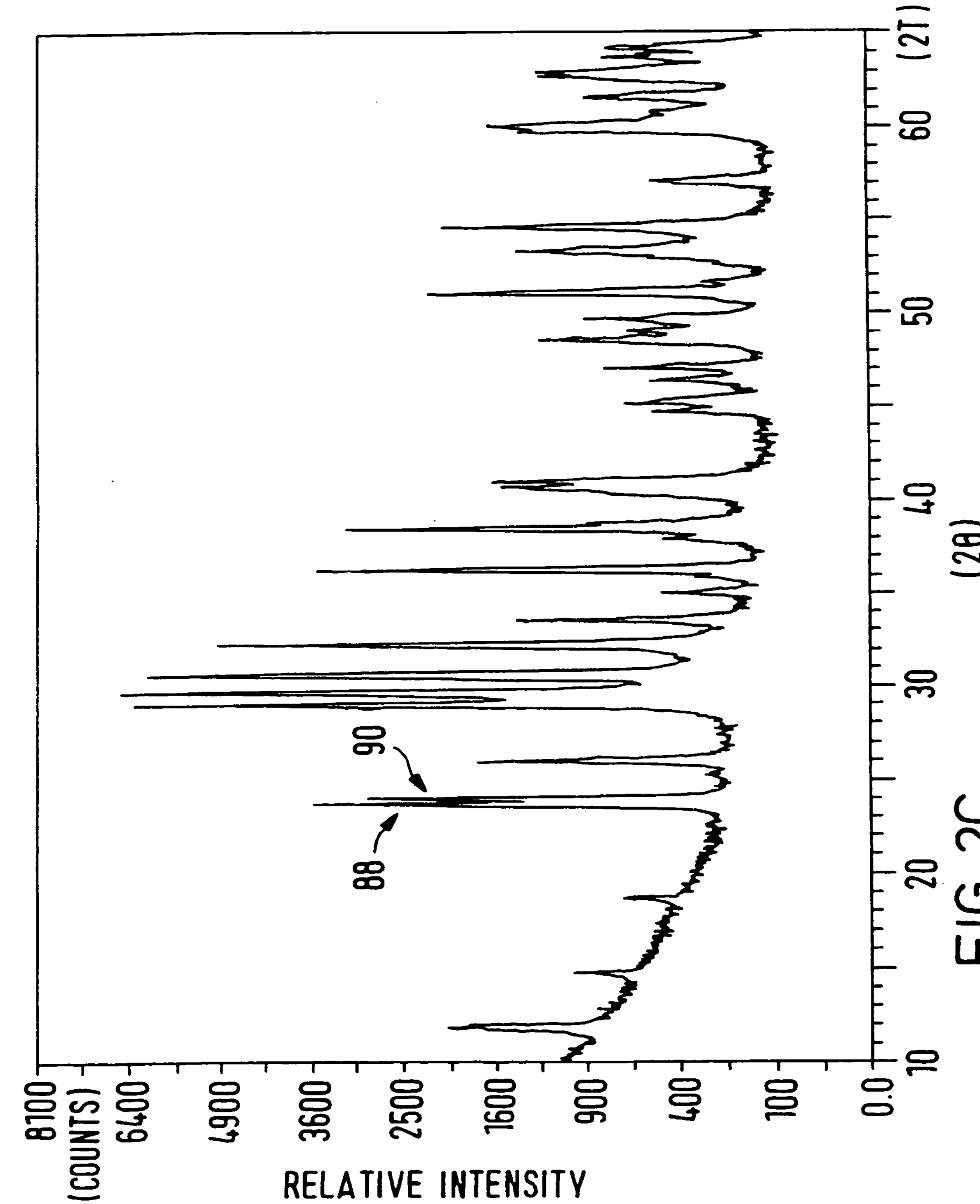
6400
4900
3600
2500
1600
900
400
100
0.0
RELATIVE INTENSITY
10
20
30
40
50
60
(2T)
(2θ)
84
86

FIG. 2B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900
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RELATIVE INTENSITY
10
20
30
40
50
60
(2T)
(2θ)
88
90

FIG. 2C

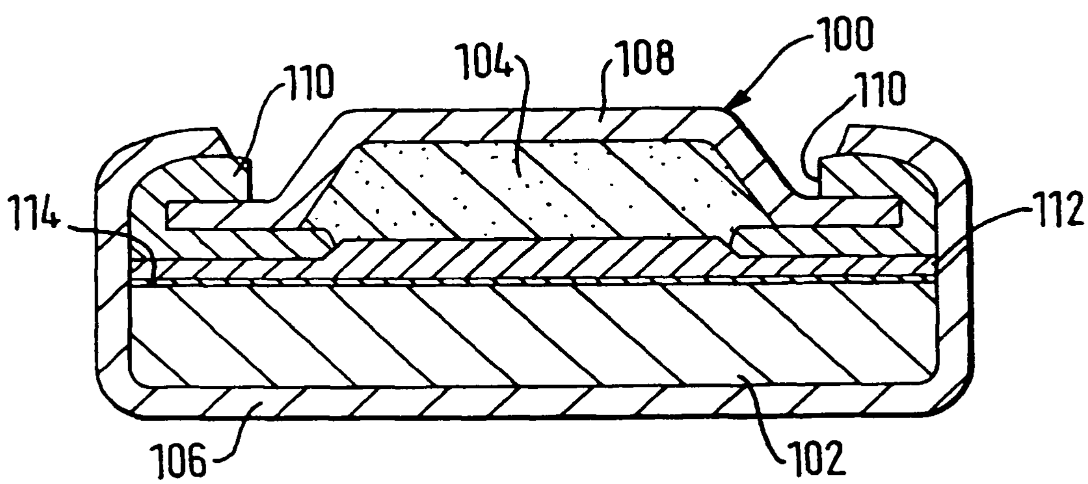

FIG. 3

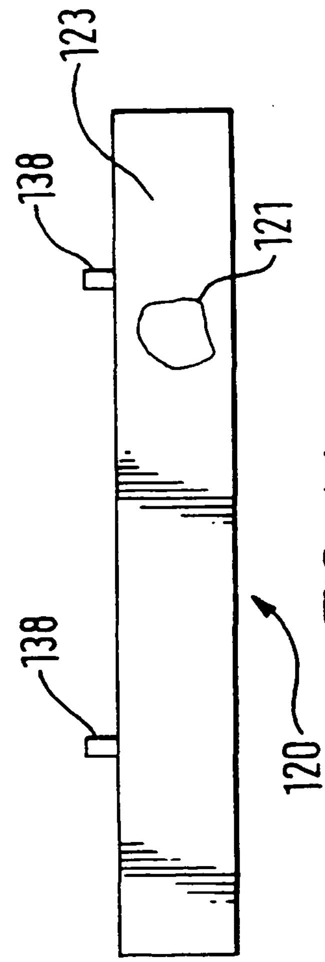

FIG. 4A

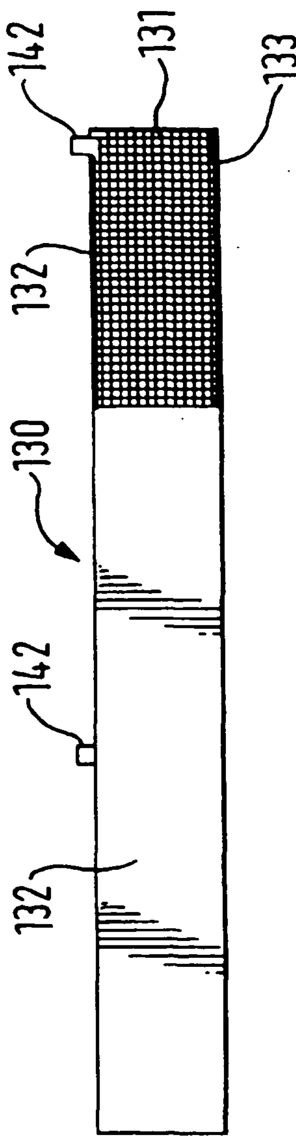

FIG. 4B

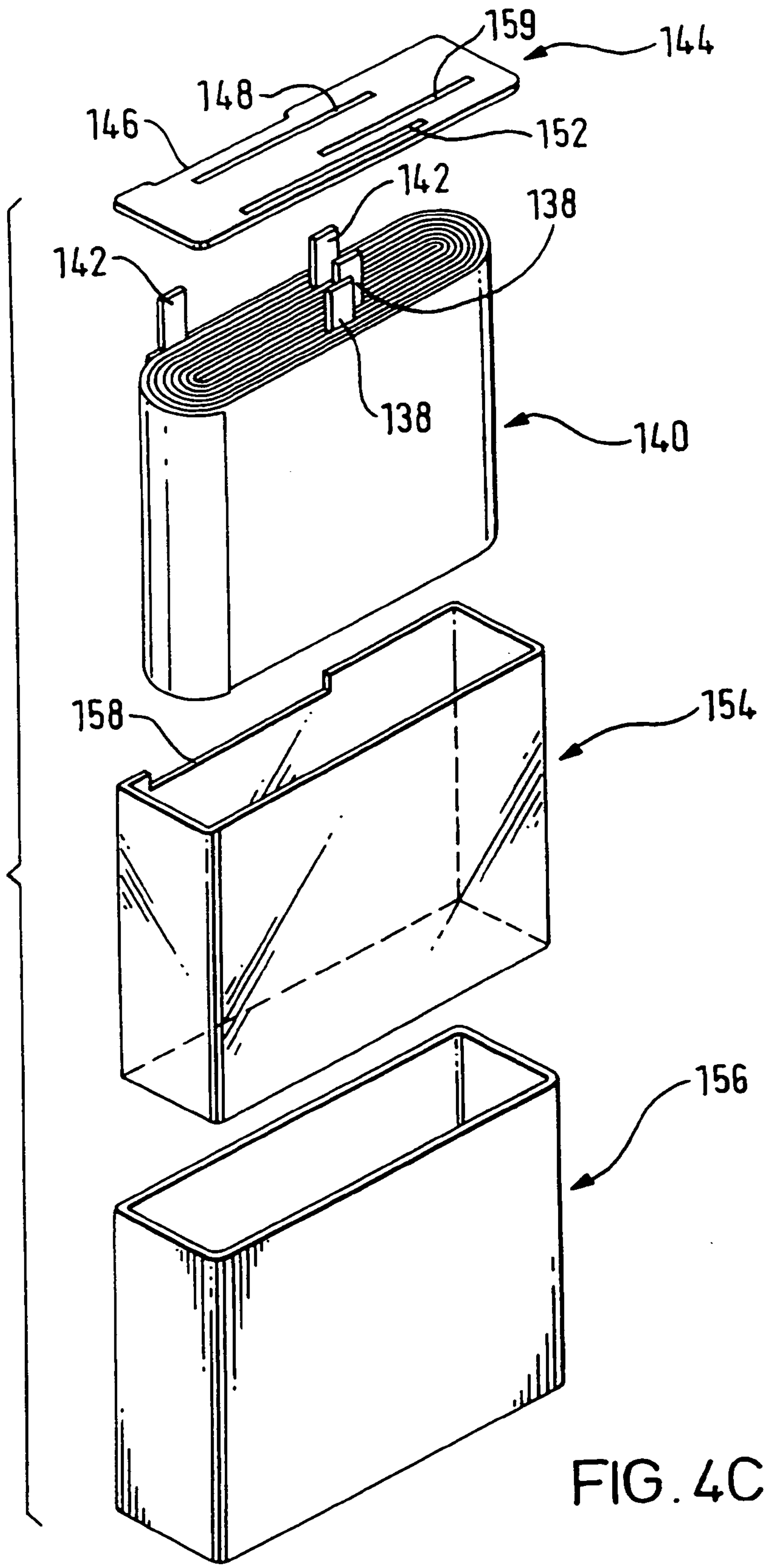

FIG. 4C

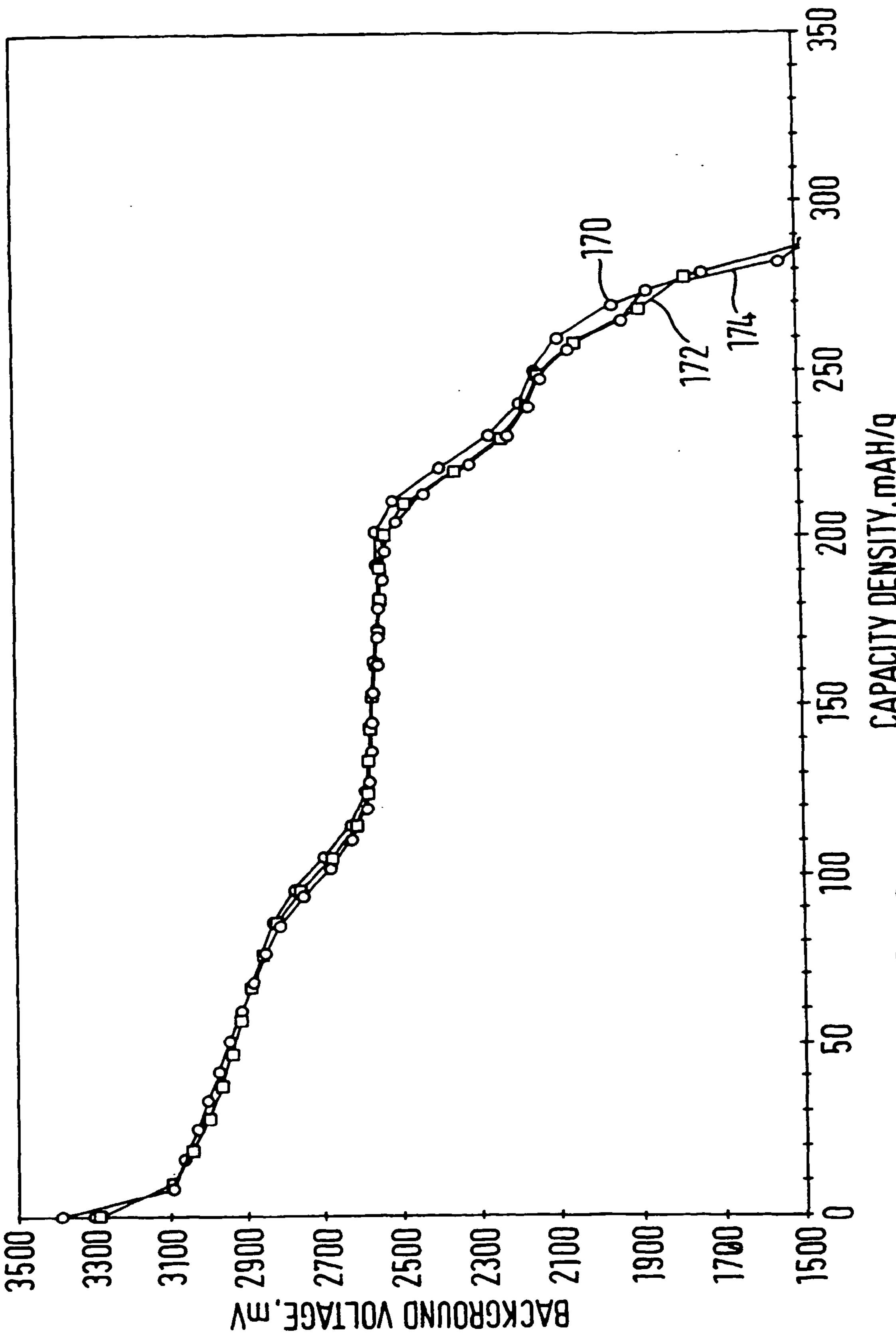
BACKGROUND VOLTAGE,mV
3500
3300
3100
2900
2700
2500
2300
2100
1900
1700
1500
CAPACITY DENSITY,mAH/g
0
50
100
150
200
250
300
350
170
172
174

FIG. 5

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 0776

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 638 946 A (GREATBATCH W LTD) 15 February 1995 * the whole document * ---	1-28	C01G31/00 H01M4/58
A	EP 0 689 256 A (GREATBATCH W LTD) 27 December 1995 * the whole document * ---	1-28	
A	EP 0 478 303 A (MEDTRONIC INC) 1 April 1992 * the whole document * -----	1-23	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C01G
H01M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	2 June 1998	LIBBERECHT, E

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